

# COMPUTERIZED PYROLYSIS MASS SPECTROMETRY OF COAL MACERAL CONCENTRATES

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## INTRODUCTION

A few pyrolysis mass spectra of purified coal maceral concentrates have appeared in the literature [1-4] showing the presence of more or less pronounced differences between the spectra of vitrinites, fusinites, sporinites and alginites. However, these studies did not attempt to distinguish between the possible effects of rank or depositional environment on the spectra and the more basic structural differences between maceral types.

Recently, the feasibility of distinguishing between these effects was demonstrated by Meuzelaar *et al.* [5,6] in a study of over 100 Rocky Mountain coal samples by Curie-point pyrolysis mass spectrometry (Py-MS) in combination with computerized multivariate statistical analysis of the data. In the present study, the same analytical approach is used to characterize a set of 30 selected maceral concentrates.

## EXPERIMENTAL

The maceral concentrates analyzed are listed in Table I. Seventeen samples originated from the maceral collection of the British National Coal Board and had been prepared by the sink/flotation method. Most of these were obtained through Dr. Given at Penn State University who redistributed these samples to different groups as part of a cooperative study [7]. Thirteen maceral concentrate fractions were prepared from two US coals by the cesium chloride gradient centrifugation method [8].

Samples were ground to 300 mesh under liquid nitrogen and 4 mg aliquots were suspended in 1 ml of methanol. Two 5 microliter drops of this suspension were coated on the ferromagnetic filaments used in Curie-point pyrolysis. A detailed description of the sample preparation and Curie-point Py-MS methods has been given elsewhere [4,6]. The Py-MS system used was an Extranuclear 5000-1 Curie-point pyrolysis MS system based on a quadrupole mass spectrometer. Experimental conditions were as follows: sample weight 20  $\mu$ g, Curie-point temperature 610°C, temperature rise time 5 s, total heating time 10 s, electron impact ionization energy 12 eV, mass range  $m/z$  20-260, scanning speed 1000 amu/s, total scanning time 25 s. All samples were analyzed in triplicate. Data processing involved the use of computerized signal averaging followed by spectrum calibration, normalization and scaling procedures. Multivariate statistical analysis, e.g. factor analysis, procedures involved the use of SPSS [9] and ARTHUR [10] program packages.

## RESULTS AND DISCUSSION

Three pyrolysis mass spectra averaged over all vitrinites, inertinites and exinites (sporinites) respectively are shown in Figure 1. The overall pattern of each maceral group agrees quite well with the spectra published by other authors [1-4], with vitrinites showing prominent phenolic series, fusinites being dominated by aromatic hydrocarbon signals and sporinites showing marked alkene peaks. More subtle differences - the significance of which can only be appreciated with the help of computerized data analysis techniques - will be discussed later.

Figure 2 shows a scatter plot of  $m/z$  110 vs. 124, two peaks known to provide a direct measure of rank in high volatile bituminous coals [5,6] and believed to represent dihydroxybenzenes and methyl-dihydroxybenzenes respectively. The peak intensities in Figure 2 indeed appear to correspond more or less directly with

carbon content and to be largely independent of maceral type. In other words, if carbon content is accepted as a measure of the rank of whole coals then a plot of  $m/z$  110 vs. 124 will reflect this rank measure in spite of possible differences in maceral composition. However, it hardly needs to be pointed out that the large differences in carbon content between macerals from the same coal (see Table I) illustrate the inadequacy of using carbon content as a coalification parameter for coals with markedly different maceral compositions.

Figure 3 shows a scatter plot of the peak intensities of  $m/z$  34 vs. 122, two peaks known to be influenced strongly by differences in depositional environment [5,6] and thought to represent hydrogen sulfide and  $C_2$ -alkylphenols respectively. In a previous study of whole coals from the US Rocky Mountain coal province the ion intensity at  $m/z$  34 was found to correlate strongly with organic sulfur content. However, in this study insufficient data were available on organic sulfur content to attempt such a correlation. Nevertheless a crude correlation appears to exist with total sulfur content. In agreement with Py-MS studies on whole coals [5] the alkylphenol peak intensities at  $m/z$  122 show a rough negative correlation with rank. Nevertheless, four of the British vitrinites show much higher peak intensity values at  $m/z$  122 than the US vitrinites of comparable rank. This is not surprising, since differences in hydroxyl content between coals from different depositional environments have also been reported [11].

Finally, the high intensity of  $m/z$  122 in the Dunsil seam inertinite, compared to the other inertinites should be noted. This is probably due to the relatively low rank of the Dunsil inertinite as well as to the fact that this sample is composed largely of semifusinite. All semifusinite-rich samples included in this study (see Table I) exhibit mass spectral patterns which tend to be intermediate between fusinites and vitrinites (compare also the two Ballarat seam samples in Figure 3) which is in agreement with presently accepted views on the origin of semifusinites from partly charred wood [12].

In view of the presence of strongly correlating series of homologous ions in all maceral spectra, as shown in Figure 1, factor analysis was performed to reduce the apparent dimensionality of the data and to bring out the major underlying chemical tendencies. The K-L plot in Figure 4 was obtained while using 80 mass peaks with highest ratio's for "between category" and "within category" variance (with each set of three replicate spectra per sample serving as a separate category). Figure 4 shows a clear separation between the three different maceral groups, with vitrinites occupying an intermediate position between fusinites and exinites. The density gradient centrifugation samples of the two US coals blend in amazingly well with the corresponding British macerals. Moreover, factor I appears to show a positive correlation with differences in sample density.

To help explain the differences in chemical composition between the three maceral groups causing the separation in Figure 4 a spectrum of the first factor, calculated according to a procedure described by Windig *et al.* [13], is shown in Figure 5. The positive component of this factor spectrum is explained by peaks with relatively high intensities in inertinites (compare with Figure 4) and is thought to represent polynuclear aromatic series with rather pronounced degrees of alkyl substitution, e.g. biphenyls and/or acenaphthenes, phenanthrenes and/or anthracenes, fluorenes, etc. The high intensity of the residual methanol solvent peak groups at  $m/z$  30-33 in inertinites may well reflect the long known correlation between the methanol absorption capacity of a coal and its degree of coalification [14]. The negative component of the factor spectrum - largely explained by peaks with relatively high intensities in the sporinite samples - shows a distinct peak pattern which we interpret as representing (poly)isoprenoids and/or related polyenic compounds. This pattern is found in all five sporinites, in spite of differences in origin, coalification stage and preparation technique. Moreover, in contrast with the more or less completely saturated or aromatized isoprenoid skeletons reported in the extractable fractions of coals and shales [15], these isoprenoid fragments liberated by Curie-point pyrolysis appear to possess a degree of unsaturation consistent with that found in many naturally occurring isoprenoids. Whether these polyenic signals are derived from carotenoid moieties in sporopollenin

[16] or perhaps from some type of fossilized natural rubber, remains open to speculation at this point. Selected peak intensities at  $m/z$  122 and 288, representing the positive (inertinite) and negative (sporinite) components of factor I respectively, are shown in Figure 6.

Although the positive portion of the factor spectrum of factor II (not shown) might be expected to provide peak patterns characteristic of vitrinites, few if any such peaks are found. In fact, factor II is dominated by an as yet unexplained series of peaks loading on the negative component and thus representing compounds which are characteristically low in vitrinites as compared to inertinites and exinites.

It may be concluded that Curie-point pyrolysis mass spectrometry in combination with multivariate statistical analysis provides valuable information on the specific chemical characteristics of coal maceral concentrates as well as on the influence of depositional environment and coalification processes. The results obtained appear to agree well with generally accepted views on the chemical nature and origin of coal macerals. Perhaps the most important new finding of this study is the presence of distinct peak patterns in sporinites which appear to represent more or less intact (poly)isoprenoid and/or related polyenic hydrocarbon moieties. More detailed accounts of these studies are being published elsewhere [6].

TABLE I  
MACERAL CONCENTRATES ANALYZED

NCB SINK/FLOTATION CONCENTRATES									
Sample			Maceral Composition (%)			Elemental Composition			
#	Code	Seam (Colliery)	VITRIN	INERT	LIPT	% C	% H	% O	% N % S <sub>t</sub>
1	T	Dunsil (Teversal)	98	1	1	81.5	5.1	10.8	2.1 1.4
2	T	ibid	6	93*	tr.	87.7	3.9	6.9	1.1 1.6
3	M	Barnsley (Markham)	3	9	8B	82.2	7.4	7.3	1.1 1.9
4	M	ibid	98	2	tr.	82.2	5.5	9.3	1.9 1.3
5	M	ibid	6	92**	1	91.6	3.6	4.1	0.4 1.2
6	W	Wheatley Lime (Woolley)	96	1	3	87.9	6.9	3.0	1.1 1.2
7	W	ibid	3	9	8B	86.5	5.6	4.9	1.8 1.4
8	A	Silkstone (Aldwarke)	0	5	95	87.2	7.4	3.6	1.2 0.7
9	A	ibid	98	1	1	86.9	5.4	4.2	1.8 1.1
10	A	ibid	5	96*	-	92.1	3.7	3.1	0.7 0.4
11	R	Ballarat (Roddymoor)	96	3	1	88.8	5.3	3.6	1.7 0.7
12	Ra	ibid	2	97	-	93.9	3.5	1.4	0.5 0.8
13	Rb	ibid	14	85*	1	91.9	4.3	3.1	0.3 0.5
14	C	Gellideg (Coegnant)	89	11	0	91.4	4.6	1.9	1.6 0.6
15	C	ibid	34	66	0	92.3	4.2	1.9	1.1 0.6
16	P	Beeston (Peckfield)	"exinite"; density 1.22 g/cm <sup>3</sup>						
17	P	ibid	"inertinite"; density 1.44 g/cm <sup>3</sup>						
U OF U DENSITY GRADIENT FRACTIONS									
Sample			Seam (Coal Field)		Density (g/cm <sup>3</sup> )		Maceral Type		
#	Code								
18	E1	Upper Elkhorn (E. Appalachian)			1.17		SPORIN		
19	E2	ibid			1.26		VITRIN		
20	E3	ibid [PSOC 2]			1.29		VITRIN		
21	E4	ibid [85.6 %C]			1.30		VITRIN		
22	E5	ibid			1.32		INERT***		
23	E6	ibid			1.36		INERT***		
24	S1	Dakota (San Juan River)			1.23		VITRIN		
25	S2	ibid			1.25		VITRIN		
26	S3	ibid			1.26		VITRIN		
27	S4	ibid [PSOC 858]			1.27		VITRIN		
28	S5	ibid [84.2 %C]			1.30		VITRIN		
29	S6	ibid			1.32		SFUSIN		
30	S7	ibid			1.38		SFUSIN		

\* semifusinite

\*\* equal amounts of fusinite and semifusinite

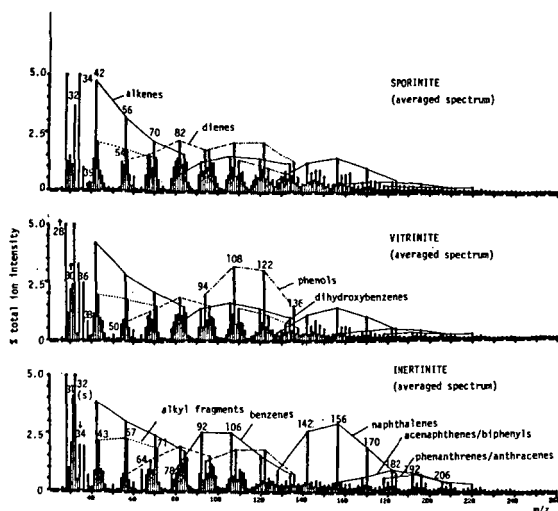
\*\*\* the parent coal (PSOC 2) contains approximately equal amounts of fusinite, semifusinite, macrinite and micrinite.

## ACKNOWLEDGEMENTS

The generous help of the British National Coal Board and the Pennsylvania State University in obtaining well characterized maceral samples is gratefully acknowledged. Furthermore, the authors are indebted to Dr. J. Karas for preparing the gradient centrifugation samples and to D.J. Davis and K.H. Wong for performing these analyses. The research reported here was sponsored by DOE grant DE FG22-80PC30242 and by matching funds from the State of Utah.

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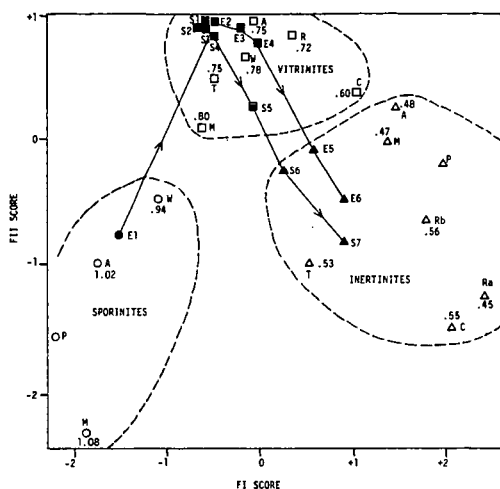


Figure 4. Karhunen Loeve plot of the first two factor scores. For explanation of symbols and codes see Figure caption 2 and Table I. US density gradient fractions are connected by arrows in order of increasing density. Numerical values ranging from .45 (Ballarat inertinite a) to 1.08 (Barnsley exinite) represent atomic H/C ratio's. Note positive correlation of factor I with density and negative correlation with H/C ratio.

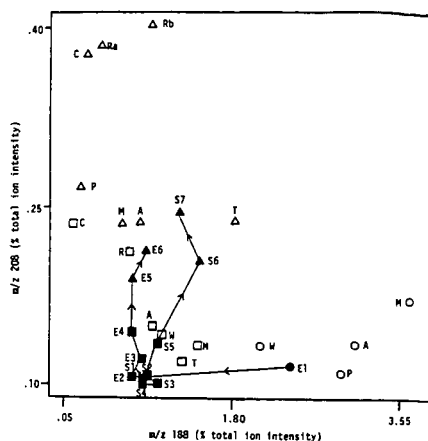


Figure 6. Scatter plot of ion intensities at  $m/z$  188 and 208 believed to represent  $C_{14}H_{20}$  polyenic and  $C_{16}H_{16}$  polynuclear aromatic hydrocarbon compounds respectively. For explanation of symbols and codes see Figure caption 2 and Table I. Comparison with Figure 5 shows that  $m/z$  208 is prominent in the positive component of Factor I whereas  $m/z$  188 is one of the highest mass peaks in the negative component.

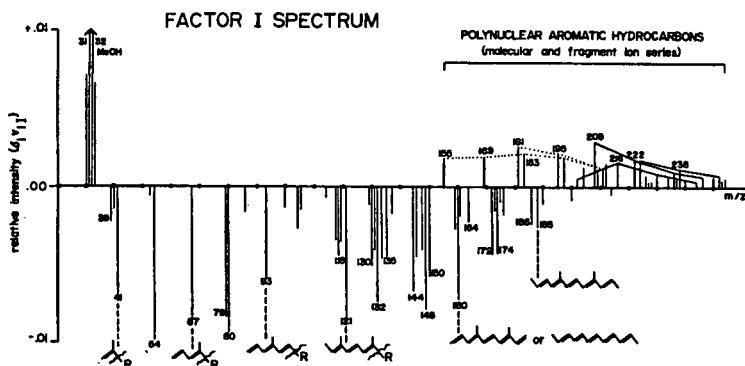


Figure 5. Factor spectrum representing factor I in Figure 4. Note marked simplification of spectral patterns as compared to Figure 1. Chemical labels are examples of possible structures only.